

Synthesis and Structures of Metal Chalcogenide Precursors

(NASA-TM-103665) SYNTHESIS AND STRUCTURES
OF METAL CHALCOGENIDE PRECURSORS (NASA)
o p CSCL 11C

N91-19296

Unclas

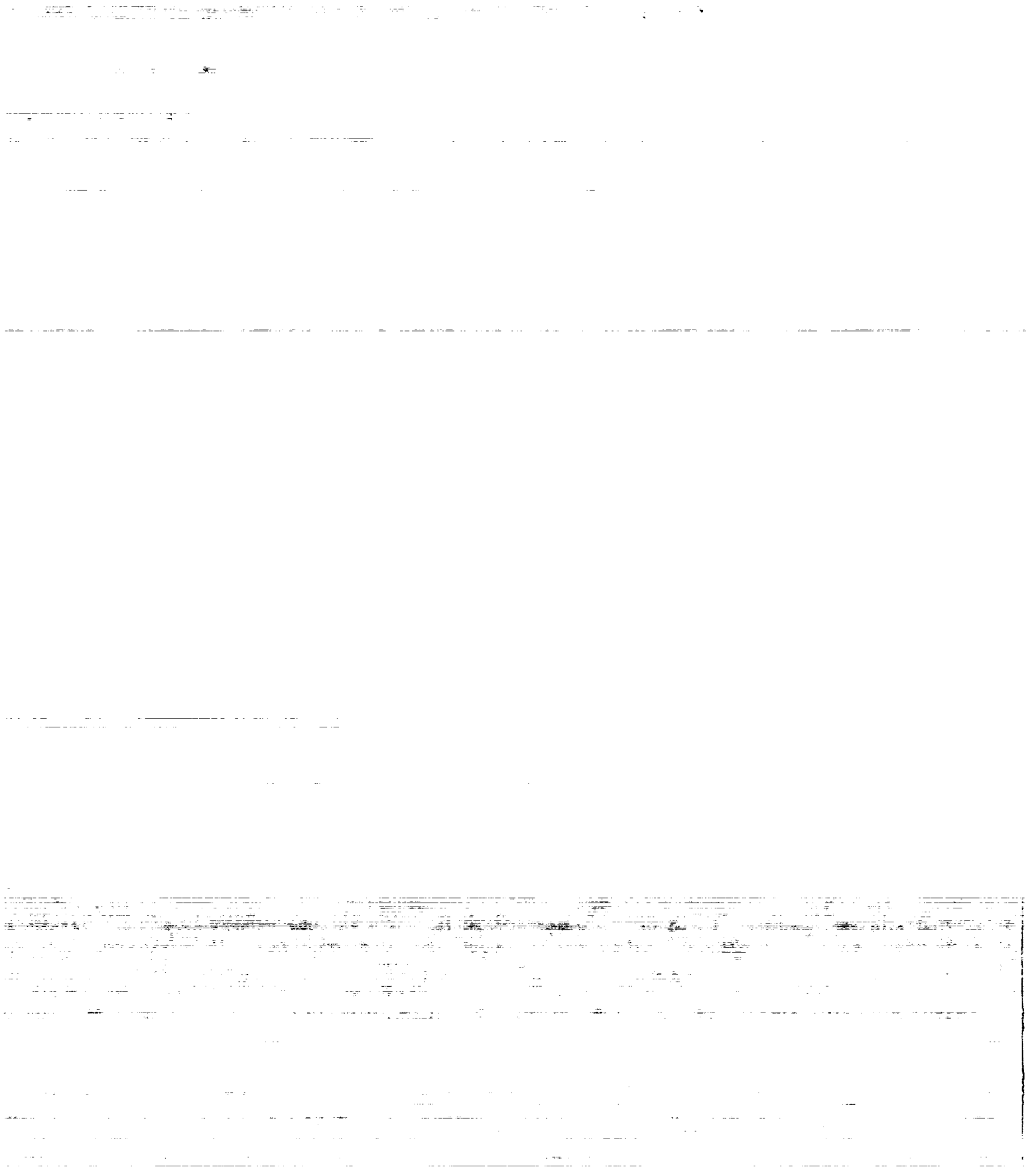
G3/27 0001699

Aloysius F. Hepp
Lewis Research Center
Cleveland, Ohio

Stan A. Duraj, Maria T. Andras,
and William E. Eckles
Cleveland State University
Cleveland, Ohio

Prepared for the
Fall Meeting of the Materials Research Society
Boston, Massachusetts, November 26—December 1, 1990

NASA



SYNTHESIS AND STRUCTURES OF METAL CHALCOGENIDE PRECURSORS

ALOYSIUS F. HEPP*, STAN A. DURAJ,** MARIA T. ANDRAS,** AND WILLIAM E. ECKLES**

* NASA Lewis Research Center, Mail Stop 302-1, Cleveland, OH 44135

** Department of Chemistry, Cleveland State University, Cleveland, OH 44115

INTRODUCTION

Applications for non-oxide metal chalcogenides are numerous. Many applications take advantage of the photoelectrical or electrical properties of these materials as solar cells (e.g. CdS and CuInSe₂); infrared detectors (e.g. Hg_{1-x}Cd_xTe and PbS) and other devices such as lasers [1]. Chevrel phases are superconducting, for example PbMo₆S₈ has a T_c of 15K [2]. An example of a chemical application is the use of heterogeneous systems such as Co-promoted molybdenum sulfide (Ni or W are sometimes substituted for Co and Mo) on γ -alumina catalysts for metal and sulfur removal under H₂ from crude oil, this allows the efficient and environmentally sound use of "dirtier" feedstocks [3]. Chemical sensitization to form AgAu_xS_y clusters on silver halide grains is an integral step in producing photographic emulsions [4]. It is interesting to note that there are many enzymes and electron transfer proteins with iron- and iron-molybdenum-sulfide cluster (e.g. ferredoxins and nitrogenase) active sites [5].

Structural and spectroscopic studies of metal chalcogenide cluster complexes enhance understanding of the chemical and electronic properties of these species in the solid state. A further motivation for this chemistry is the possible invention of novel precursors for solid state materials [6], with potentially improved properties. While there is tremendous activity and interest in the chemistry of compounds containing metal-sulfur, selenium, and tellurium bonds [7-9], the chemistry of electron deficient transition and main group metals is relatively underdeveloped. Our interest in species relevant to hydrodesulfurization catalysis led us to explore the reactivity of early transition metal sandwich complexes with sulfur-rich molecules such as dithiocarboxylic acids [10] and is continuing towards preparation of mixed metal sulfide complexes.

We have recently initiated work on precursors to CuInSe₂ and related chalcopyrite semiconductors. The very high radiation tolerance and the high absorption coefficient of CuInSe₂ makes this material extremely attractive for lightweight space solar cells. The potential for low-cost, high power-to-weight ratio, radiation resistant space solar cells has led to renewed interest in chalcopyrite semiconductors. We describe synthesis and structures of In- and Cu-chalcogenide complexes, and routes to precursors, illustrating our approach with an example from earlier work [10].

EXPERIMENTAL

All manipulations of moisture and air-sensitive materials were done under an inert atmosphere by standard Schlenk techniques on a double-manifold vacuum line or in a Vacuum Atmospheres Co. glovebox equipped with a HE-493 dri-train. Solvents were freshly distilled from benzophenone ketyl prior to use. The metal sandwich compounds and CH₃CSSH were synthesized as described in [10]. Metal compounds and powders were obtained from Strem Chemicals, Newburyport, MA. Chalcogenide-containing compounds were obtained from Aldrich Chemical Co., Milwaukee, WI. Electron impact mass spectra were recorded on a Finnigan TSQ-45 mass spectrometer. Single-crystal x-ray analyses, were done on an Enraf-Nonius CAD-4 diffractometer.

RESULTS AND DISCUSSION

$(\eta^6\text{-C}_6\text{H}_6)_2\text{V}$ reacts with excess CH_3CSSH in toluene at 25°C for 4 days to produce $[(\text{CH}_3\text{CS}_2)_2\text{V}(\mu\text{-}\eta^2\text{-S}_2)_2\text{V}(\text{S}_2\text{CCH}_3)_2]$, **1**, in yields up to 62 % (figure 1). Brown crystals were grown by layering a benzene solution of **1** with heptane. The molecule crystallizes in the monoclinic space group, $\text{P}2_1/\text{c}$; with cell constants of $a = 10.425(2) \text{ \AA}$, $b = 11.123(2) \text{ \AA}$, $c = 9.133(4) \text{ \AA}$, $\beta = 97.12(2)^\circ$; cell volume, $V = 1051(1) \text{ \AA}^3$; and two molecules in the unit cell. An ORTEP diagram of **1** is shown in figure 1.

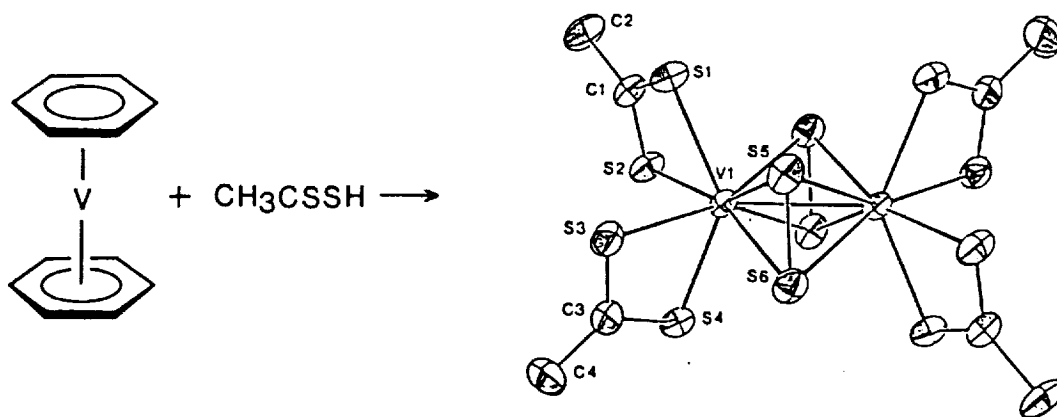


Figure 1. Chemical reaction leading to formation of **1**. ORTEP drawings of **1** also defines the labelling scheme. The thermal ellipsoids enclose 50% of electron density.

Magnetic susceptibility and structural data is consistent with a single bond between vanadium atoms with a V-V distance of 2.800 \AA ; the compound is diamagnetic as expected for a $d^1\text{-}d^1$ unit. The V-V bond distance is nearly the same as the V-V bond distance in the tightly bound $\text{V}(\mu\text{-}\eta^2\text{-S}_2)_2\text{V}'$ unit (V-V distance of 2.83 \AA [11]) in the mineral patronite, $(\text{VS}_4)_n$ and is similar to a recently described V-V compound prepared from VS_4^{3-} and a dithiuram disulfide derivative (V-V distance of 2.85 \AA [12]). The stability of the V_2S_4 core in **3** is evidenced by the identification of V_2S_4^+ in the mass spectrum (70 eV, solid probe). The facile reaction between $(\eta^6\text{-C}_6\text{H}_6)_2\text{V}$ and the sulfur-rich dithioacetic acid illustrates the potential utility of this approach to produce new metal-sulfide compounds. We have extended this chemistry to include several dithiocarboxylic acids and other low-valent metal compounds and metal powders including Cu, In, Zr, V, Hf, and Ta powders; InCl , Ga_2Cl_4 , and related halides; and other early transition metal sandwich compounds of Ti, Zr, V, and Nb [10,13].

Chemistry with other chalcogenide-rich molecules is under investigation to produce precursors for chalcopyrite semiconductors. In order to deposit thin films of metal chalcogenides on lightweight substrates such as polymers, low temperature chemical vapor deposition of volatile species must be employed. Further, to enhance control of stoichiometry it is desirable to use single-molecule precursors; this is one goal of our current research effort. Part of this effort entails the development of relevant aspects of In-, Ga-, and Cu-chalcogenide coordination and organometallic chemistry. Our approach is at all times to determine the structures of new intermediate or analogous compounds to enhance our understanding of the synthetic chemistry of precursor formation and to apply this understanding to the decomposition of candidate precursors.

Other chalcogenide-rich chemistry that is under investigation uses known oxidants like dialkyl- or diaryldichalcogenides and dithiuram derivatives, REER (E = S or Se, and R = $-\text{CH}_3$, $-\text{C}_6\text{H}_5$, or $-\text{CH}_2\text{C}_6\text{H}_5$; E = S; R = $-\text{C}(\text{S})(\text{NR}_2)$). Reactions were generally carried out under inert atmosphere in coordinating

solvents. One example of a recently characterized compound is shown in figure 2. $\text{Trans-Cl}_2\text{In}(\text{S-C}_6\text{H}_5)(\text{NC}_5\text{H}_4\text{CH}_3)_3$, 2, is synthesized from simple starting materials producing clear rectangular prismatic crystals. The molecule crystallized in the monoclinic space group, $P2_1/n$; with cell constants of $a = 9.620(1) \text{ \AA}$, $b = 17.601(5) \text{ \AA}$, $c = 14.197(4) \text{ \AA}$, $\beta = 99.28(2)^\circ$; cell volume, $V = 2372(4) \text{ \AA}^3$; and four molecules to the unit cell.

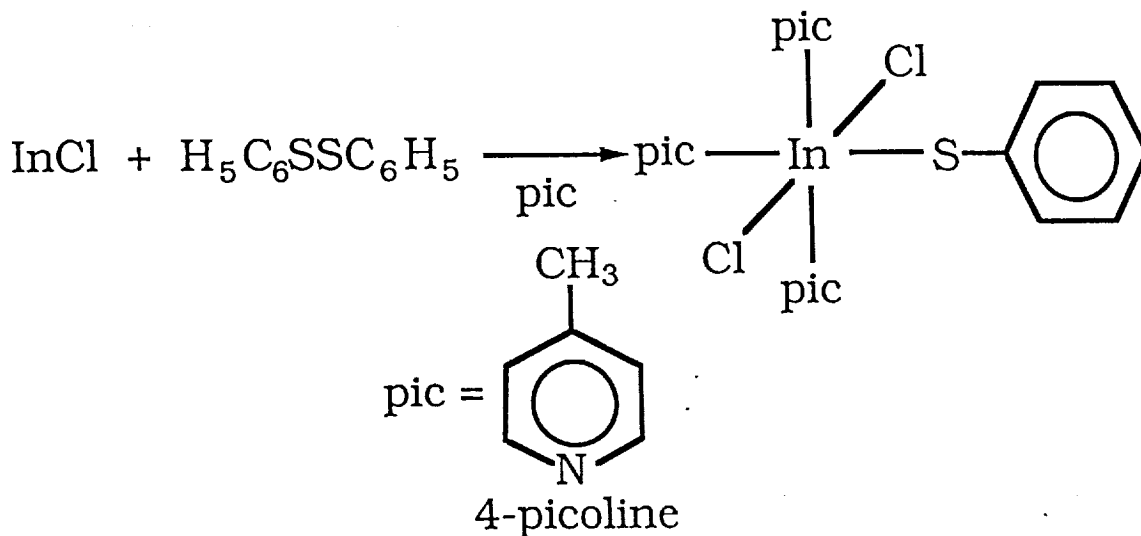


Figure 2. Chemical reaction leading to formation of 2. Diagram of 2 is shown on the right of the figure.

There are a number of synthetic studies of REER to prepare new compounds [14,15]. While similar compounds have been reported, this is the first structure of an indium compound with this coordination environment that has been determined. This molecule is easy to prepare and has five sites, two chlorides and three solvent ligands, for further chemistry. We have also prepared analogous compounds using different metals (Ga, Cu), ligands (-ER), and solvents. Reactions in tetrahydrofuran between metal powders and a dithiuram derivative produces black crystalline material after layering. X-ray diffraction studies failed to detect the presence of any metal sulfides. While it is known that dithiuram reacts with metal powders, no structures were reported [16]; we were only able to identify a known Ni complex [17]. We are currently investigating the structure of these molecules; the reaction chemistry to form precursors is currently underway.

CONCLUSIONS

The use of low-valent π -bonded sandwich compounds and dithiocarboxylic acids as starting materials to prepare metal sulfur-containing complexes is novel and shows the potential for the development of facile syntheses of new metal sulfide compounds. We are currently extending this approach in two ways: using other chalcogenide-rich reactants with other low-valent metal complexes and metal powders. Precursors synthesized will be evaluated for the purity, morphology, and electrical properties of the materials produced.

ACKNOWLEDGEMENTS

S.A.D. and M.T.A. acknowledge support from the Petroleum Research Fund, a Research Creative Activity Award (Cleveland State University) and a

Research Challenge Grant (Ohio Board of Regents). S.A.D. acknowledges partial support from NASA grant NCC 3-162. A.F.H. acknowledges support from the Director's Discretionary Fund at NASA Lewis. We thank Dr. P. Kibala and Prof. F.A. Cotton, Texas A&M University, for x-ray structural analysis of 1.

REFERENCES

- [1] L.L. Kazmerski and S. Wagner, in Current Topic in Photovoltaics, edited by T.J. Coutts and J.D. Meakin (Academic Press, New York, 1985), pg. 41.
- [2] R. Chevrel and M. Sargent, Top. Curr. Phys. 32, 25 (1982).
- [3] O. Weisser and S. Landa, Sulphide Catalysts, Their Properties and Applications (Pergamon Press, New York, 1973).
- [4] D.A. Pitt, M.L. Rachu, and M.R.V. Sahyun, Photogr. Sci. Eng. 25, 57 (1981).
- [5] F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 5th ed. (John Wiley and Sons, New York, 1988), pg. 1335.
- [6] E. Ramli, T.B. Rauchfuss, and C.L. Stern, J. Am. Chem. Soc. 112, 4043 (1990).
- [7] A. Müller, Polyhedron 5, 323 (1986).
- [8] M. Rakowski DuBois, Chem. Rev. 89, 1 (1989).
- [7] M. Draganjac and T.B. Rauchfuss, Angew. Chem. Int. Ed. Eng. 24, 742 (1985).
- [8] A. Müller and E. Diemann, Adv. Inorg. Chem. 31, 89 (1987).
- [9] J. Wachter, Angew. Chem. Int. Ed. Eng. 28, 1613 (1989).
- [10] S.A. Duraj, M.T. Andras, and B. Rihter, Polyhedron 8, 2763 (1989); S.A. Duraj, M.T. Andras, and P.T. Kibala, Inorg. Chem. 29, 1232 (1990); M.T. Andras, Ph.D. Thesis, Cleveland State University, 1990.
- [11] R. Allman, I. Baumann, A. Kutoglu, H. Rosch, and E. Hellner, Naturwissenschaften 51, 263 (1964).
- [12] T.R. Halbert, L.L. Hutchings, R. Rhodes, and E.I. Stiefel, J. Am. Chem. Soc. 108, 6437 (1986).
- [13] S.A. Duraj, A.F. Hepp, M.T. Andras, W.E. Eckles, J.A. Schupp, R.A. Martuch, and E.B. Clark, unpublished results.
- [14] A. Boardman, S.E. Jeffs, R.W.H. Small, and I.J. Worrall, Inorg. Chim. Acta 83, L39 (1984).
- [15] R. Kumar, H.E. Mabrouk, and D.G. Tuck, J. Chem. Soc., Dalton Trans., 1045 (1988); T.A. Annan, R. Kumar, H.E. Mabrouk, D.G. Tuck, and R.K. Chadha, Polyhedron 8, 865 (1989).
- [16] T. Tetsumi, M. Sumi, M. Tanaka, and T. Shano, Polyhedron 5, 707 (1986).
- [17] See the following extensive reviews: D. Coucouvanis, Prog. Inorg. Chem. 11, 233 (1970); D. Coucouvanis, Prog. Inorg. Chem. 26, 301 (1979).

Report Documentation Page

1. Report No. NASA TM-103665		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Synthesis and Structures of Metal Chalcogenide Precursors				5. Report Date	
				6. Performing Organization Code	
7. Author(s) Aloysius F. Hepp, Stan A. Duraj, Maria T. Andras, and William E. Eckles				8. Performing Organization Report No. E-5872	
				10. Work Unit No. 307-51-00	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191				11. Contract or Grant No.	
				13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546-0001				14. Sponsoring Agency Code	
15. Supplementary Notes Prepared for the Fall Meeting of the Materials Research Society, Boston, Massachusetts, November 26—December 1, 1990. Aloysius F. Hepp, NASA Lewis Research Center. Stan A. Duraj, Maria T. Andras, and William E. Eckles, Cleveland State University, Cleveland, Ohio					
16. Abstract Applications for non-oxide metal chalcogenides are numerous. Solid state applications include solar cells (e.g. CdS and CuInSe ₂); infrared detectors (e.g. Hg _{1-x} Cd _x Te and PbS) and other devices such as lasers. Chevrel phases are examples of metal sulfides with interesting electrical properties; PbMo ₆ S ₈ is a superconductor with a T _c of 15K. Metal sulfides are used as hydrodesulfurization catalysts and chemical sensitizers for photographic film. They are also found at the active site of several electron transfer proteins and enzymes. Structural and spectroscopic studies of metal chalcogenide cluster complexes enhance understanding of the chemical and electronic properties of these species in the solid state. A further motivation for this chemistry is the possible invention of novel precursors for solid state materials, with potentially improved properties. Our interest in species relevant to hydrodesulfurization catalysis led us to explore the reactivity of early transition metal sandwich complexes with sulfur-rich molecules such dithiocarboxylic acids. We have recently initiated work on precursors to CuInSe ₂ and related chalcopyrite semiconductors. The very high radiation tolerance and the high absorption coefficient of CuInSe ₂ makes this material extremely attractive for lightweight space solar cells. Our general approach in early transition metal chemistry, the reaction of low-valent metal complexes or metal powders with sulfur- and selenium-rich compounds, has been extended to the synthesis of chalcopyrite precursors. We describe synthesis, structures and routes to single-molecule precursors to metal chalcogenides.					
17. Key Words (Suggested by Author(s)) Chalcopyrite semiconductors; Low-temperature processing; Metal selenides; Metal sulfides; Dithiocarbamates			18. Distribution Statement Unclassified - Unlimited Subject Category 27		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of pages 5	22. Price* A02		

